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REACTION OF POTASSIUM PEROXIDE WITH CARBON DIOXIDE

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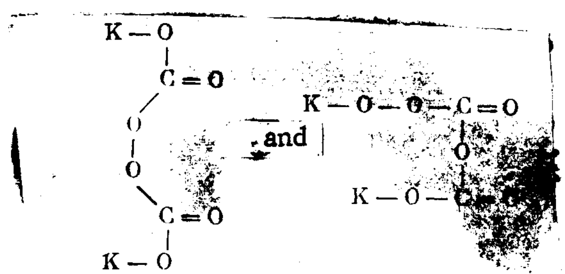
ABSTRACT. The authors discuss the composition of final products produced by the reaction of KO_2, potassium peroxide, with CO_2, carbon dioxide, in continuous determination of the phase composition during carbonation, as best carried out under close to thermal conditions. The formation of K_2CO_4 from KO_2 is accelerated with rising temperature, but decomposition is also correspondingly accelerated.

INTRODUCTION

Harcourt /1/, Fritz and Mayer /2/ showed that the reaction of potassium tetroxide with carbon dioxide at 100-120° forms only K_2CO_3 according to the equation: /370*

$$K_2O_4 + CO_2 \rightarrow K_2CO_3 + 1.5\,O_2.$$

Riesenfeld and Mau /3/, carrying out the same process in an ethyl alcohol medium at 0-5°, obtained well-formed crystals of potassium percarbonate with the composition $K_2C_2O_6$. In its behavior toward a KI solution, this compound differed from $K_2C_2O_6$, obtained by electrolysis of concentrated K_2CO_3 solutions, in that it evolved one-third as much iodine. This fact led to the hypothesis that two structural isomers with different positions of oxygen exist:



Since $K_2C_2O_6$ decomposes in accordance with the equation $2K_2C_2O_6 \rightarrow 2K_2CO_3 + 2CO_2 + O_2$ even on slight heating, the formation of this compound at high temperatures obviously should not be expected. Direct action of K_2CO_3 on liquid CO_2 according to Cailletet /4/ leads to the formation of $K_2C_2O_5$, which sometimes is also incorrectly called potassium percarbonate.

*Numbers in the margin indicate pagination in foreign text.

In all of the indicated studies, the authors did not investigate the kinetics of the process, and determined only the composition of the final products without trying to establish the formation of intermediate compounds.

EXPERIMENTAL

The study of the reaction of K_2O_4, or more correctly, KO_2, with CO_2, with a continuous determination of the phase composition during carbonation, is best carried out under close to isothermal conditions. For this reason, special measures should be taken in order to record the exothermic effect in such a range that there is no sharp increase in temperature at the gas-solid phase interface and that no conditions are created for the decomposition of the substances formed. To this end, special studies were undertaken with different delivery rates of CO_2 in a small cylindrical reactor having a porous bottom, /371
with various particle sizes and heights of the KO_2 layer at constant temperatures of the surrounding medium of 0, 10, 25 and 50°.

It was found that at 0°, for a height of the granular KO_2 layer ($d \cong 1.0$ mm) of 1-2 mm and a weight of 0.5 g at a CO_2 delivery rate of 0.1-0.2 l/hr, an adequate isothermicity of the carbonation process was achieved as the temperature in the KO_2 layer rose by no more than 0.3-0.5°. A further increase of the CO_2 delivery rate immediately caused a marked overheating; thus for example, at 0.3 l/hr the overheating was 10°, at 0.5 l/hr, 20°, and 1.0 l/hr, 50°. This is plainly illustrated by the diagram in Figure 1. Therefore, in further studies use was made of minimum rates of CO_2, which caused only a slight heating up of the KO_2 layer and hence insured an adequate isothermicity of the process. At different time invervals ranging from 1 hour to 1200 hr, the samples studied were analyzed for the content of active oxygen, carbon dioxide, and potassium. The data of the analyses were converted and plotted on a triangular diagram K_2O-CO_2-0.5 O_2, on which the direction and sequence of the change of KO_2 composition in the course of the carbonation could be determined. In this representation, the compositions of the possible peroxides, carbonates and percarbonates of potassium were clearly defined on the diagram. All the representatives of potassium percarbonates from the standpoint of their total composition could be regarded as products of successive addition of oxygen to potassium carbonates K_2CO_3 and $K_2C_2O_5$ or of CO_2 to potassium peroxides K_2O_2, K_2O_3 and K_2O_4 (if the earlier representation of the formulas of potassium peroxides is retained

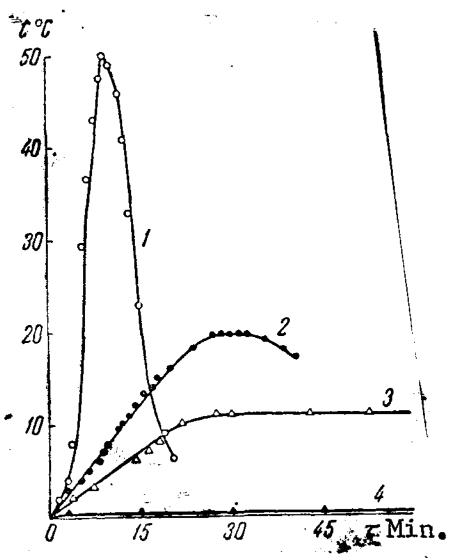


Figure 1. Delivery rate of CO_2: 1- 1 l/hr; 2- 0.5 l/hr; 3- 0.3 l/1 hr; 4- 0/1 l/hr for a layer height of 2 mm.

and K_2O_3 is not considered to be the chemical compound $2KO_2.K_2O_2$). As a result, the possible representatives of potassium percarbonates on the diagram are determined by the position of the figurative points situated at the cross section of the tie lines potassium carbonates - oxygen and potassium peroxides - carbon dioxide.

Thus, a direct addition of CO_2 to potassium peroxide may yield the following compounds:

CO_2 and K_2O_4 yield $K_2O_4.CO_2$ and $K_2O_4.2CO_2$, i.e., K_2CO_6 and $K_2C_2O_8$;
CO_2 and K_2O_3 yield $K_2O_3.CO_3$ and $K_2O_3.2CO_2$, i.e., K_2CO_5 and $K_2C_2O_7$;
CO_2 and K_2O_2 yield $K_2O_2.CO_2$ and $K_2O_2.2CO_2$, i.e., K_2CO_4 and $K_2C_2O_6$.

Of the possible representatives of potassium percarbonates shown on the diagram, only one compound, $K_2C_2O_6$, has been obtained and described earlier. All the remaining representatives of potassium percarbonates were unknown. It should be noted that by reacting CO_2 with sodium peroxide at 8°, Wolffenstein and Peltner (5) obtained the compound Na_2CO_4, which was patented by the Merck Company (6). The same compound was also obtained by Blankart (7) by the reaction: /372

$$COCl_2+Na_2O_2 \rightarrow Na_2CO_4+2NaCl+0,5O_2$$

Data on the Change of the Chemical Composition of KO_2 in the Course of Carbonation at 0, 10, 25, and 50°.

Sequence Number	Time/hours	Temperature, °C: 0			10			25			50		
		% 0,5 O_2	% CO_2	% K_2O	% 0,5 O_2	% CO_2	% K_2O	% 0,5 O_2	% CO_2	% K_2O	% 0,5 O_2	% CO_2	% K_2O
1	0	31,2	1,4	67,4	31,2	1,4	67,4	31,2	1,4	67,4	31,2	1,4	67,4
2	1	—	—	—	—	—	—	—	—	—	29,2	4,8	66,0
3	3	28,5	4,9	66,6	27,5	6,4	66,1	26,8	7,3	65,9	17,7	17,8	64,5
4	13	—	—	—	—	—	—	24,1	10,8	65,1	9,4	26,6	64,0
5	30	—	—	—	—	—	—	23,1	12,0	64,9	5,2	30,7	64,1
6	40	26,1	8,8	65,1	—	—	—	—	—	—	—	—	—
7	55	—	—	—	23,2	11,3	65,5	20,4	14,3	65,3	3,9	31,5	64,6
8	80	—	—	—	—	—	—	17,6	17,1	65,3	—	—	—
9	110	22,9	12,3	64,8	—	—	—	14,4	21,2	64,4	—	—	—
10	170	—	—	—	—	—	—	12,6	23,4	64,0	—	—	—
11	200	20,7	14,2	65,1	17,2	18,2	64,6	—	—	—	1,6	32,0	66,4
12	250	—	—	—	14,5	—	—	—	—	—	—	—	—
13	310	—	—	—	12,7	23,3	64,0	10,8	25,9	63,3	—	—	—
14	360	18,8	16,1	65,1	12,6	23,7	63,7	—	—	—	—	—	—
15	465	—	—	—	12,3	26,2	61,5	9,4	27,3	63,3	—	—	—
16	520	15,6	19,7	64,7	—	—	—	—	—	—	—	—	—
17	620	13,6	22,8	63,6	—	—	—	8,8	27,7	63,5	—	—	—
18	720	12,3	23,6	64,1	7,6	42,0	50,4	4,7	31,6	63,7	—	—	—
19	840	10,3	—	—	3,2	45,0	51,8	—	—	—	—	—	—
20	940	9,1	29,3	61,6	0,6	47,5	51,9	—	—	—	—	—	—
21	1000	5,0	46,1	48,9	—	—	—	—	—	—	—	—	—
22	1140	1,0	47,3	51,7	—	—	—	—	—	—	—	—	—
23	1240	0,3	47,9	51,8	—	—	—		—	—	—	—	—

Experimental Data

The results of studies of the carbonation of KO_2 at 0, 10, 25 and 50° are collected in the table, and the data obtained were used to plot diagrams 2, 3, 4 and 5. The carbon dioxide used had been thoroughly dried and supplied at a rate of ~0.2 l/hr, KO_2 was in the form of grains with d≃1.0 mm with a layer height of ~2mm.

In Figure 2, the left portion of diagram $K_2O - 0.5O_2 - CO_2$ shows a gradual change of the chemical composition of K_2O_4 as the carbonation process proceeds. At first, a straight line of up to 940 hr and then a gentle curve with a slight inflection run from the initial composition of K_2O_4 to the figurative point of K_2CO_4. This is followed after 980 hr by a sharp break up to the composition $K_2C_2O_6$ and a new change of direction up to $K_2C_2O_5$, which is reached after 1300 hr. A similar course is shown by the kinetic curve plotted in the right portion of the diagram as a function of time in a projection on the line $0.5\ O_2$-CO_2. The presence of three branches shows up very distinctly.

This gradual change of the chemical composition of the initial product K_2O_4 involves the following successive reactions:

$K_2O_4+CO_2 \rightarrow K_2CO_4+O_2$, with a change from yellow to pink color; /373
$K_2CO_4+CO_2 \rightarrow K_2C_2O_6$, white color
$K_2C_2O_6 \rightarrow K_2C_2O_5+0.5\ O_2$

i.e., in accord with the first branch of the diagram; the reaction of K_2O_4 with CO_2 forms the previously unknown compound K_2CO_4, analogous to Na_2CO_4, oxygen being evolved. The phase composition of point 20 is very close to the composition of K_2CO_4.

The percarbonate K_2CO_4, formed in a relatively short time inverval, adds CO_2 and converts into $K_2C_2O_6$ without splitting off oxygen; $K_2C_2O_6$ is a well-known compound which was obtained earlier by Riesenfeld and Mau. This percarbonate splits off oxygen and thus converts into the compound $K_2C_2O_5$, which may be regarded as dehydrated potassium bicarbonate, in accordance with the equation

$$2KHCO_3 \rightarrow K_2C_2O_5 + H_2O$$

which may be termed potassium pyrocarbonate. The latter, $K_2C_2O_5$, is completely stable at 0°.

In general, the diagram (Fig. 3) for 10° is of the same form as the diagram for 0°, the difference being that under equilibrium conditions, the position up to the figurative point $K_2C_2O_6$ is not reached. The process of conversion of K_2CO_4 into $K_2C_2O_6$ by the direct addition of carbon dioxide does not go to completion, and at point 18, an oxygen decomposition takes place with the formation of potassium pyrocarbonate.

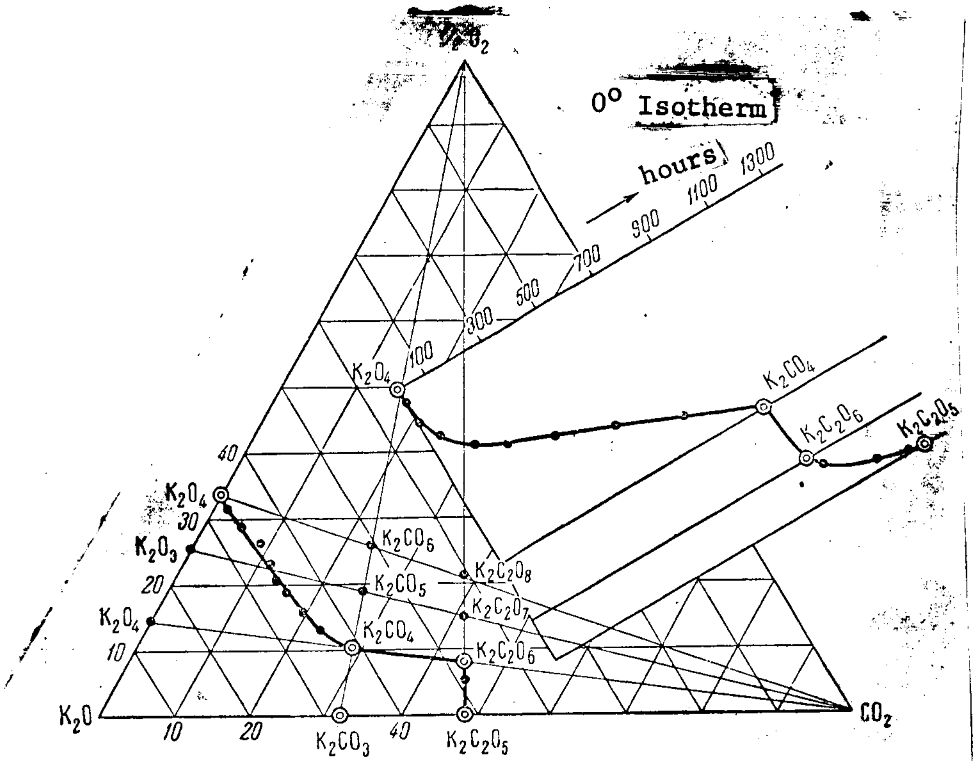


Figure 2.

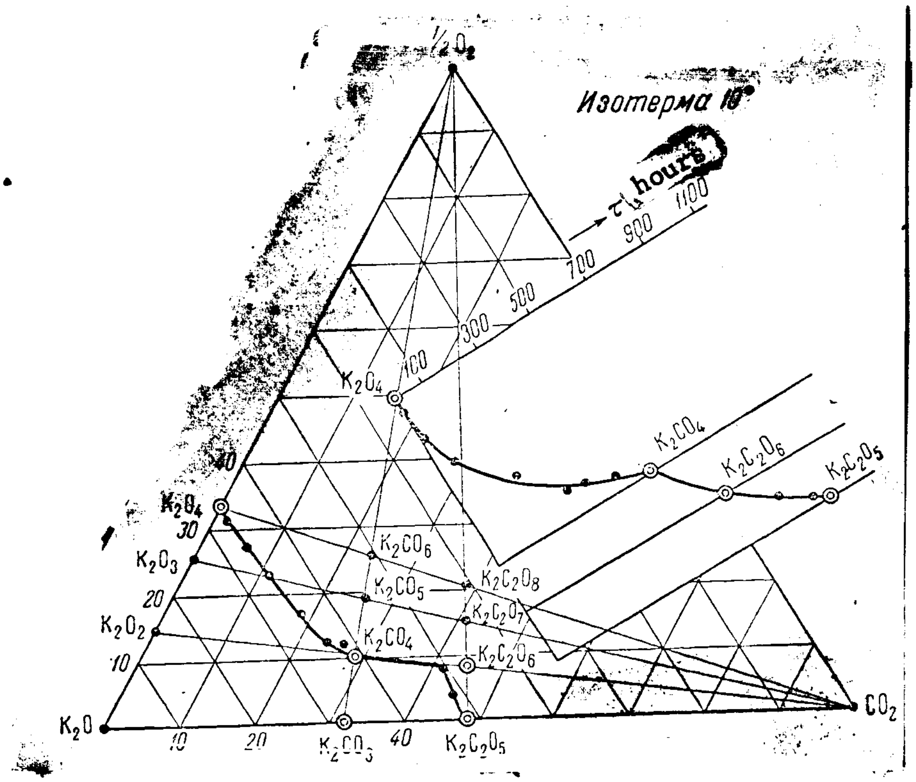


Figure 3.

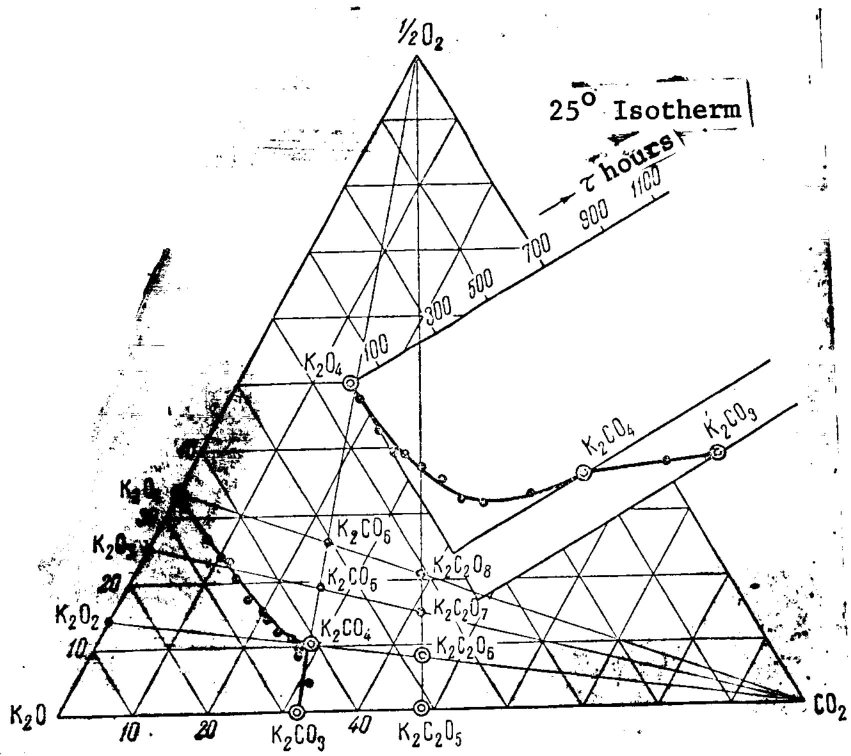


Figure 4.

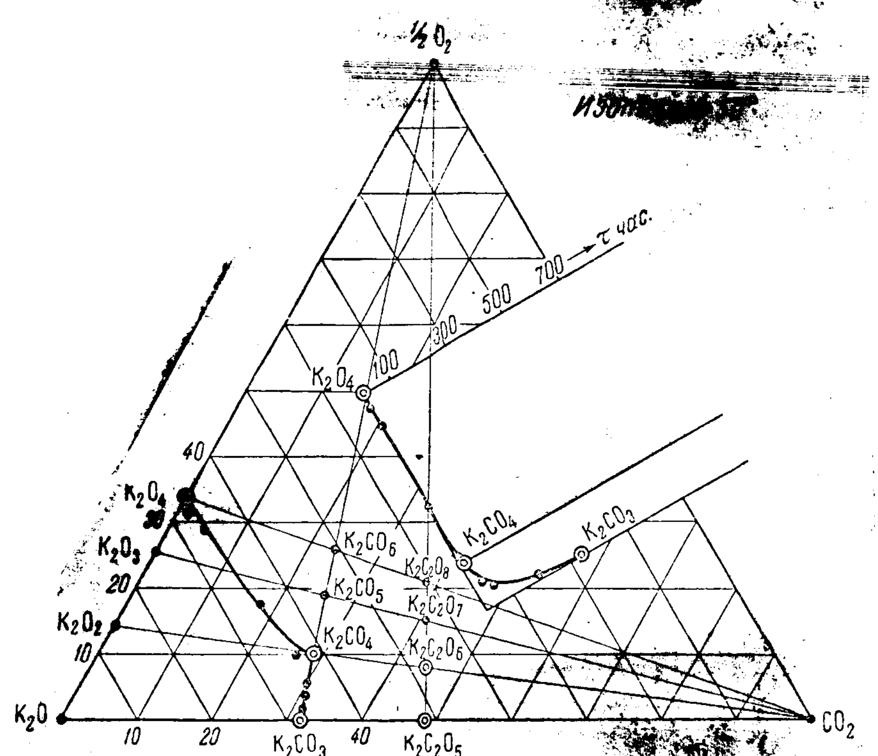


Figure 5.

The diagrams of Figures 4 and 5 for 25 and 50° are much simpler. The branches of the conversion $K_2CO_4 \rightarrow K_2C_2O_6$ and $K_2C_2O_6 \rightarrow K_2C_2O_5$ are absent, indicating the instability of $K_2C_2O_6$ and $K_2C_2O_5$ at these temperatures. At 25 and 50°, the process of carbonation K_2O_4 is accompanied by only two reactions:

$$K_2O_4 + CO_2 \rightarrow K_2CO_4 + O_2$$

and

$$K_2CO_4 \rightarrow K_2CO_3 + 0{,}5\ O_2.$$

As follows from an analysis of the kinetic curves, both of these reactions accelerate appreciably with rising temperature: the formation of K_2CO_4 at 0° is achieved after 940 hr; at 10°, after 550 hr; at 25°, after 460 hr, and at 50° after 13 hr.

CONCLUSION

1. It was found that at 0 and 10°, the reaction of KO_2 K_2O_4 and CO_2 proceeds in three stages:

$$K_2O_4 + CO_2 \rightarrow K_2CO_4 + O_2; \quad (1)$$
$$K_2CO_4 + CO_2 \rightarrow K_2C_2O_6 \quad (2)$$
$$K_2C_2O_6 \rightarrow K_2C_2O_5 + 0{,}5\ O_2. \quad (3)$$

2. According to reaction 1, when oxygen splits off, a new compound which has not been described in the literature is formed, namely potassium percarbonate, of the composition K_2CO_4, which is stable over a wide temperature range.

3. By directly adding CO_2 at temperatures of 0 and 10°, potassium percarbonate is converted in accordance with reaction 2 into a well-known compound, $K_2C_2O_6$, which further decomposes in accordance with reaction 3, evolving oxygen and forming the compound $K_2C_2O_5$, i.e., potassium pyrocarbonate.

4. At 25 and 50°, the compounds $K_2C_2O_6$ and $K_2C_2O_5$, which are rich in CO_2, do not form. The process of decomposition of K_2CO_4 in a CO_2 atmosphere is associated with the evolution of oxygen and formation of potassium carbonate K_2CO_3. /376

5. The formation of K_2CO_4 from KO_2 is substantially accelerated with rising temperature, but its subsequent decomposition is also correspondingly accelerated.

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